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PHOTO-INDUCED HOMOLYSIS OF ALKYLTRICYCLOPENTADIENYL-URANIUM(IV) COMPLEXES: AN EXAMPLE OF A SUCCESSFUL $U^{IV} \rightarrow U^{III}$ REDUCTION

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Summary

Photo-induced reduction of two organouranium complexes of the type Cp_3UR (R = CH_3 and n-C_4H_9) was studied in toluene and THF solution at various temperatures. Optimal conditions for the production of $Cp_3U \cdot THF$ as the final product involve UV/VIS irradiation in THF at ca. 60°C. Spin trap experiments indicate that, at least in THF, intermediate free radicals participate. The results, including gas chromatographic, mass spectroscopic and ^1H NMR spectroscopic measurements, are discussed in terms of a virtually first order multi-step process involving discrete radical pairs kept together efficiently by solvent cages so that H-atom abstraction from a Cp ligand followed by decomposition of the organometallic product is largely avoided.

Introduction

Reduction of organometallic U^{IV} compounds of the type Cp_3UX (Cp = η^5-C_5H_5; X = Cp [1] or Cl [2—4] leading to the U^{III}-systems Cp_3U or $Cp_3U \cdot THF$ requires relatively strong reductants ***. Nevertheless, a few reports indicate that

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*** An example of exceptionally an facile reduction is provided by the decomposition of the assumed reaction intermediate $\{[C_5(CH_3)_5]_2U^{IV}HCl\}$ into $\{[C_5(CH_3)_5]_2U^{III}Cl\}_3$ [5], while uranocene, $(C_8H_8)_2U^{IV}$, strongly resists reduction to $[(C_8H_8)_2U^{III}]^-$ [6].

the photolysis of U^{IV} systems could also lead to U^{III} derivatives, although probably with low quantum yields 7—9. Marks and co-workers have shown that the related Th^{IV} compound $Cp_3Th(i\text{-}C_3H_7)$ can be readily photolysed to give good yields of the dark-green complex "Cp_3Th" [10] * as well as propane and propene (approximately 1/1). A β-hydride elimination mechanism was considered to be an essential step in this reaction, and more recent evidence for a corresponding photo-reduction was found for the photolysis of $Cp_3Th(n\text{-}C_4H_9)$ and even $Cp_3U(n\text{-}C_3H_7)$ [12].

As trivalent uranium is more stable than trivalent thorium, the present study was undertaken with the aim of demonstrating the formation of U^{III} derivatives from various alkyltricyclopentadienyluranium complexes under photolytic conditions, and to provide a better understanding of the cleavage of the uranium—alkyl σ-bond. As first candidates for such systematic photochemical investigations involving particularly variations of the solvent and the reaction temperature as well as spin trap experiments and kinetic studies, the two alkyl complexes Cp_3UCH_3 (I) and $Cp_3U(n\text{-}C_4H_9)$ (II) were chosen. While II should also be susceptible to β-hydride elimination, I should favour typical homolytic bond cleavage.

Experimental

All operations were conducted under a strict inert gas (N_2 or Ar) atmosphere adopting carefully purified solvents devoid of even traces of O_2 and H_2O. The two starting complexes I and II were prepared by published procedures [14] involving reaction of the appropriate alkyllithium with Cp_3UCl [16] in THF at —70°C. The purity of the Cp_3UR complex was checked by ^1H NMR and NIR/VIS spectroscopy. In a series of experiments, the filtered THF solutions of I or II were immediately subjected to photolysis.

^1H NMR spectra were recorded mainly at room temperature on a Varian NV 14 spectrometer (CW) operating at 60 MHz. One resonance of internal THF was chosen as a locking signal, the large shifts of the samples induced by their paramagnetism allowing the use of non-deuterated THF. All the shifts quoted are referred to benzene (with upfield shifts positive).

Optical spectra were run on a Cary 17 spectrometer. Rapid switching from NMR to NIR/VIS spectroscopy was made possible by attacking a special NMR tube in place of the usual stopper of the NIR/VIS cell.

Gas chromatographic (GC) analyses were performed on a Perkin—Elmer mode 3920 B equipped with a squalane 5 m column (1 mm diameter) operating between room temperature and 100°C. Gaseous samples were collected above the solution and introduced through the septum with a gas syringe. The H/D ratios of hydrocarbons resulting in THF-d_8 solution were determined from their mass spectra obtained on a VG 305 F mass spectrometer with a resolution sufficient to discriminate between the fragments OH^+ and CH_3D^+.

A typical experiment was performed as follows: A portion from a ca. 10^{-2} *M*

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* By a different route, Kanellakopulos et al. have arrived at a deeply purple product of the same composition "Cp_3Th" [11]; intense studies on the nature of the dark-green and purple species are in progress [12,13].

stock solution of Cp_3UR in THF was transferred into a UV/VIS cell or NMR tube of Pyrex glass which was placed into a thermostated water bath together with a corresponding reference cell. The latter was kept in the dark to distinguish genuine photolytic from common thermal effects. The sample in the Pyrex flask was exposed to the light of a 500 W mercury lamp through a 15 cm cell filled with water to filter out the IR emission (distance: ca. 10 cm; average irradiation time: <45 min). Gas evolution was observed throughout the irradiation period.

For the spin trap experiments a cylindrical quartz tube (4 mm diameter) was degassed on a vacuum line over at least three freeze-pump cycles and poorly filled with a saturated solution of the spin trap reagent in toluene or THF. After adding a solution of I or II in the same solvent (final concentration: 10^{-3} to 10^{-2} *M*, depending on the experiment) the tube was sealed and immediately placed into an ER-400 X-RL cavity of a Bruker ER 420 ESR-spectrometer equipped with B-ST 100/700, B-MN 12, and B-A6 accessories for temperature variation, magnetic field calibration and frequency measurements, respectively.

Irradiation was carried out during the ESR experiment with a Hanovia 977 B-0090 1000 W Hg/Xe arc lamp in a Schoeffel lamp housing LH 15 1 H, with the light focussed through quartz lenses, flowing water (15 cm) and Corning 3-73 (420 nm) or Pyrex filters. Owing to the rapid reaction of the spin trap with the sample at elevated temperatures (> 40°C), accompanied by substantial precipitate formation, spin trap experiments were only successful between 0 and 20°C, and not at the temperature of optimal radical generation. The spin trap reagents adopted were 5,5'-dimethylpyrrolidine-*N*-oxide (DMPO), nitrosodurene (ND), and phenyl-*N*-t-butylnitrone (PBN), in approximately 10^{-2} *M* concentrations.

Results

Optimal solvent, temperature and light. We found that in benzene, toluene or acetonitrile, the irradiation of Cp_3UR usually gives rise to insoluble dark products and residual solutions devoid of any new ^1H NMR resonances. Hence most of our photolytic experiments were carried out in THF. The choice of THF represents an important variation in view of the fact that the photolysis of the corresponding Cp_3ThR systems [10,12] can be readily conducted in benzene.

Another important observation was that efficient photolysis takes place only at elevated temperature (above 40°C); hence most of our experiments were carried out at 60°C. While at 0°C practically no variation of the starting samples was detectable over a period of several hours, the half reaction time $t_{1/2}$ of I, monitored by NMR and/or by GC, amounts to 10 ± 2 h at 20°C and reaches about one tenth of that value around 40°C. Typically, the $t_{1/2}$ values in THF of irradiated samples and of the corresponding reference samples in the dark differ by at least one order of magnitude (e.g. at 60°C: 40 min and 500 min, respectively). In view of the previously reported comparatively slow ($t_{1/2}$ at 97°C > 10^3 h [14]) thermolytic cleavage of the U—C σ-bond in toluene solution, even the thermal stabilities of I and II turn out to be considerably lower in THF than in toluene.

It is also noteworthy that relatively good yields (up to 70%) of $Cp_3U \cdot THF$ are obtained only if the ultraviolet portion of the irradiated light is not filtered

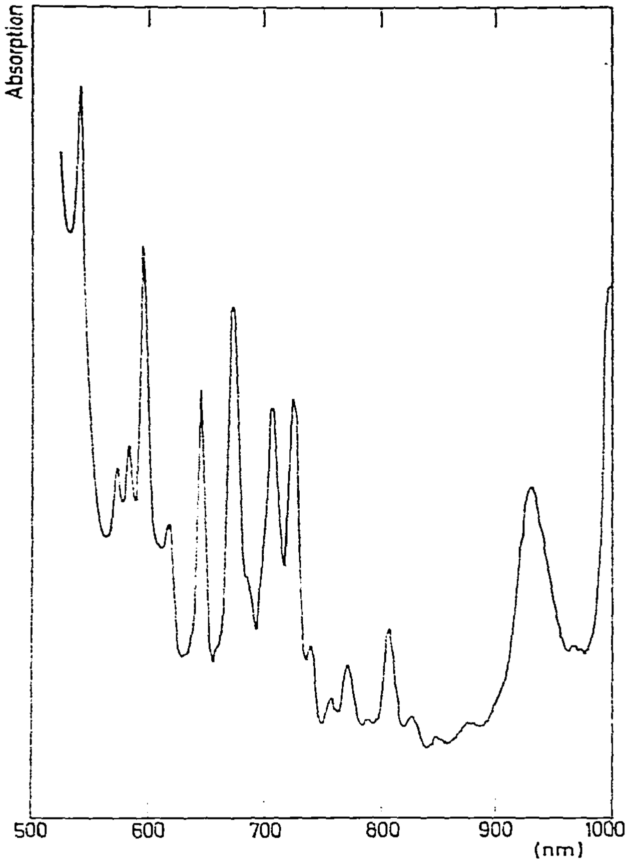

Fig. 1. Absorption spectrum of $Cp_3U(n\text{-}C_4H_9)$, solvent: THF; room temperature.

out (60°C in THF). Actually, Cp_3UR systems start absorbing light with large extinction coefficients ($\epsilon > 10^3$) even above 20 000 cm^{-1} (Fig. 1) suggesting possible absorption by the solvent also. Apart from the common need for UV light, the photolytic conditions for Cp_3UR differ thus markedly from those reported for the photo-reduction of Cp_3ThR [10] (i.e. almost quantitative reaction in benzene solution at 5°C within 1—2 h). Thus, the specific photo-reduction of Cp_3UR under the conditions chosen by us must undoubtedly be considered as resulting from the concerted influence of the solvent, light and temperature.

Nature of the hydrocarbons evolved. Complete GC analyses of the atmosphere above the irradiated solutions of II and I, (THF, 60°C) have revealed that the main products from II are butane and butene (ca. 93/7), and from I mostly methane. Elemental hydrogen was not observed. The butane/butene ratio is practically constant at various stages of the photolysis. There is no noticeable change in the gaseous products if toluene is used instead of THF.

Reference samples of II in toluene kept in the dark at 60°C yielded butane and butene (75/25), which differs from the ratio 92/2 reported by Marks et al. [14] for the same solvent, but at a higher temperature (97°C). Complex I gave

80% of methane and about 20% of ethane. Our GC results thus appear virtually similar to those reported by Marks et al. for the pure thermolysis in toluene solution. The dark thermolysis of solid I, however, give different results in that the methane/ethane ratio clearly decreases with temperature yielding even more ethane than methane at 120°C.

A mass spectroscopic analysis of the gaseous decomposition products from I was undertaken mainly to elucidate the origin of the hydrogen atom used to form methane. Thus pure thermolysis in THF-d_8 gave rise to a CH_3D/CH_4 ratio of 30/70, whereas the reverse ratio (i.e. 70/30) was found under irradiation. Thermolysis of Cp_3UR in toluene-d_8 is reported to give RD proportions varying only between 9.0 (R = n-propyl) and 4.2% (R = *trans*-2-butenyl) [14]. It appears therefore that the change in solvent causes only moderate deviations from the highly preferred hydrogen abstraction from one Cp ligand observed for pure thermolysis in aromatic solvents, while the additional influence of light clearly favours the solvent as an efficient source of H atoms. On the other hand, only ca. 4% of the propene produced during the photo-reduction of $Cp_3Th(i\text{-}C_3H_7)$ is reported not to originate from the isopropyl ligand [10].

Kinetics. Essential features of the kinetics were evaluated from the relative intensities of representative proton resonances of I or II, and of the GC signals of methane and butane, respectively, as observed at various stages of the reaction. The well-consistent NMR and GC results indicate that the reaction is of first order with respect to the Cp_3UR concentration (Fig. 2). The same reaction order was found for the pure thermolysis of Cp_3UR compounds in toluene [14], suggesting unimolecular cleavage of the U—C σ-bond under both sets of conditions

Spin trap experiments. All spin trap experiments conducted before, during, and immediately after, the photolysis of I and II in toluene (room temperature) in the presence of either of the three reagents (vide supra) showed no evidence of alkyl radicals. These results are in fair accord with the extremely high stereospecificity of the pure thermolysis [14], which implies that relatively long-lived radicals or radical pairs in sufficient concentrations are rather unlikely. Without irradiation, only weak signals, assumed to be indicative of adducts with Cp$^•$ radicals were observed, and these disappeared, or decreased, on exposure to light. In view of the facile formation of trigonal bipyramidal complexes of the type

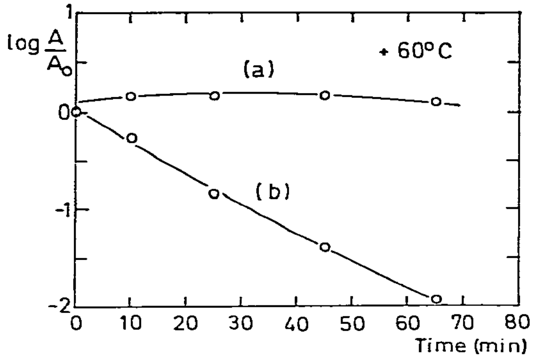

Fig. 2. Plot of log A/A_0 vs. time (A/A_0 = intensity ratio of characteristic ^{1}H-NMR signals (area) during and before the reaction, respectively) of complex I. Curve (a), purely thermal reaction; b, photolysis.

Cp_3UXY [16], the formation of corresponding Cp_3UR adducts with the spin trap followed by a release of Cp· radicals cannot be ruled out.

The ESR pattern tentatively attributed to an adduct of the spin trap ND and a Cp· radical in THF and in toluene consists of six equally intense lines (Fig. 3). The parameters a_N and a_H, respectively, are 13.56 and 6.22 G in THF and 15.5 and 5.6 G in toluene. A sextet is consistent with the expectation of a primary triplet each component of which is further split into a doublet. Our findings differ from those of Tsai and Brubaker, who clearly confirmed the appearance of a 1/2/2/1 quartet of equidistant lines ($a_N = a_H = 13.0$ G) during the photolysis of the complex Cp_2TiCl_2 in various solvents [17]. Although this discrepancy is at present not fully understood, an assignment of the sextet observed by us in terms of any trapped radical originating from a THF molecule seems very unlikely, as the same type of ESR spectrum occurs in both THF and toluene.

On irradiation only, and with PBN as spin trap, THF solutions of complex II show neat ESR patterns characteristic of an n-butyl radical spin adduct (g 2.0073 G; a_N 13.87 G; a_H 11.01 G). Complex I shows under the same conditions a signal indicative of a methyl radical spin adduct the intensity of which, however, does not markedly decrease in the absence of light. With ND instead of PBN, a purely thermal reaction is again indicated by the appearance of a Cp· radical adduct. Under photolytic conditions, the lines characteristic of methyl and n-butyl free radicals, respectively, are superimposed on the signals of the assumed Cp·/ND-adduct.

Fig. 4 illustrates the influence of irradiation on complex I in THF solution

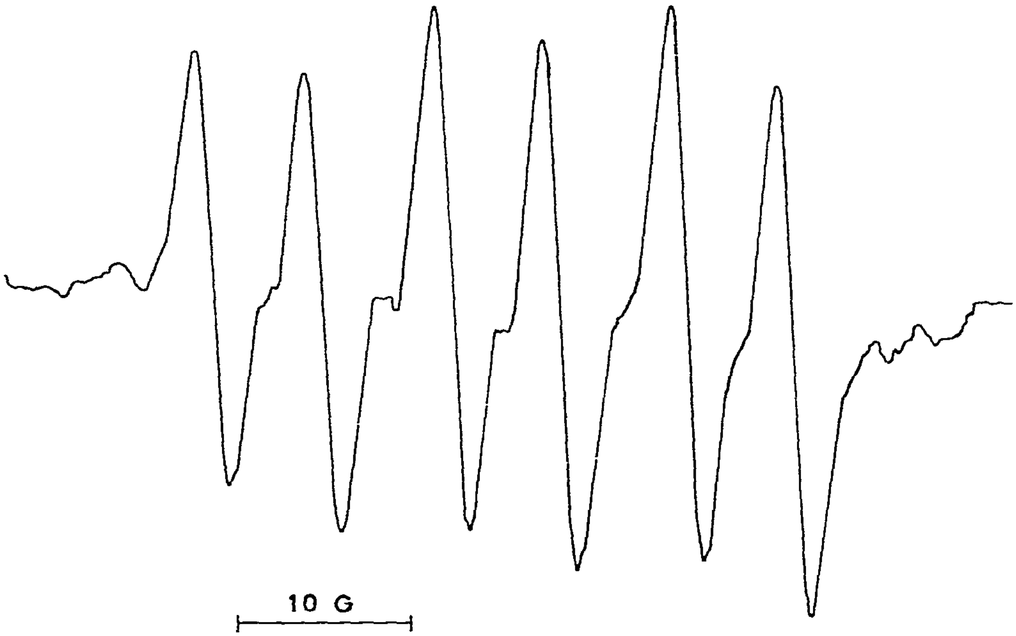

Fig. 3. ESR-spectrum of non-irradiated $Cp_3U(n\text{-}C_4H_9)$ (ca. 2×10^{-2} M, THF, room temperature) in the presence of spin trap ND (microwave frequency 9749 MHz; modulation intensity 1.0 X 1 G; signal gain 4×10^5; power 83 mW).

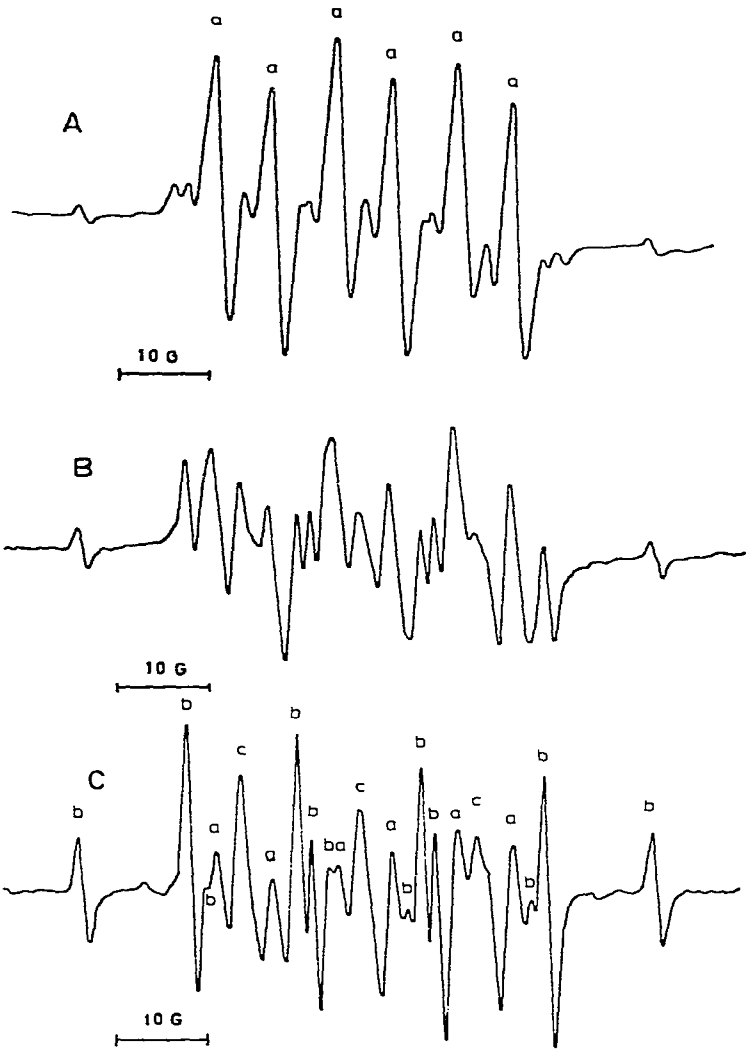

Fig. 4. ESR-spectra of Cp_3UCH_3 (3×10^{-2} *M*, THF) in the presence of spin trap ND at different stages of the photolysis. A: before irradiation (microwave frequency 9465 MHz; modulation intensity 0.8×1 G; receiver gain 2.0×10^5; power 23 mW). B: after 5 min of irradiation (9465 MHz; 0.4×1 G; 4.0×10^5; 42 mW). C: after 30 min of irradiation (9469 MHz; 1.0×1 G; 4.0×10^5; 7.8 mW). Lines attributed to $Cp^{\bullet}$ are signified by (a); lines attributed to $CH_3^{\bullet}$ by (b).

and in the presence of ND. In spectrum A of a non-irradiated solution, the lines of $Cp^{\bullet}$ (a) clearly dominate over those from a small amount of $CH_3^{\bullet}$ (b). Spectra B and C demonstrate that after 5.0 and 30 min, respectively, of irradiation the concentration of CH_3 radicals has increased at the expense of that of $Cp^{\bullet}$ (CH_3-radical: g 2.0071; a_N 13.78 G; a_H 12.13 G). Towards the end of the photolysis, a third type of spin trap adduct becomes apparent as a 1/1/1 triplet (g 2.0076; a_N 13.06 G) which might be tentatively attributed to an adduct "$Cp_3{}^{238}U^{III}$–ND" (or rather "$Cp_3{}^{238}U^{IV}$–ND"), as ^{238}U has no nuclear spin to couple with the unpaired electron (Fig. 4, C).

The concentration of the sample influences the trap experiments slightly in that at low concentrations the alkyl radical is readily detectable whereas at higher concentrations (corresponding to a larger ratio sample/spin trap) the ND adduct with the Cp· radical becomes predominant. This observation is in accordance with the above-mentioned suggestion of labile substrate/spin trap adducts as a major source of Cp· radicals.

With DPPH (diphenylpicrylhydrazine) as a calibration standard, the spin density exclusively attributable to free alkyl radicals generated by irradiation is estimated to be of the order of 0.01% of the Cp_3UR concentration. In view of this comparatively low value, it is important to point out that for technical reasons (vide supra) the measurement was restricted to 22°C and irradiation with a Corning 3-73 filter ($\lambda > 420$ nm), while optimal U—C δ bond cleavage occurs above 40°C, and with the UV light present (Pyrex filter).

Nature of the resulting organouranium system(s). Apart from their utility for the monitoring of the cleavage of the U—C σ-bond, ^1H NMR spectra were also used to identify the resulting organouranium systems successively detectable in THF solution. The first new signal to occur during the photolysis of both I and II lies at 15.5 ppm (Cp_3UR: ca. 10 ppm [14,19]), which by its position and line width is reminiscent of the intermediate "species A" observed during the reduction of Cp_3UCl with $LiAlH_4$ [3]. Its optical absorption spectrum can be attributed to a U^{IV} species which has been tentatively suggested to be a soluble form of the hydride complex "Cp_3UH" [3].

Next, a somewhat broader signal at 20.5 ppm appears, corresponding possibly to the "species B" of ref. 3, which must be due to the first U^{III} derivative. While the proton resonance of Cp_3U (prepared from active uranium metal and cyclopentadiene) has been reported to occur only 10.5 ppm upfield from benzene [20], the corresponding resonances of adducts with Lewis bases [1] may be found at considerably higher fields [13]. As the photolysis reaches completion after a few hours, a brown solid precipitates from the solution, making it impossible to observe the expected resonance corresponding to "species C" at ca. 28 ppm [3]. However the brown product has been clearly identified as the adduct $Cp_3U \cdot THF$ by comparing its vibrational and NIR/VIS absorption spectra with various data from previous experiments. The mass spectrum (100°C, 72 eV) displays intense signals of the molecular ion, $Cp_3U(THF)^+$, and of the fragments Cp_3U^+, Cp_2U^+, CpU^+ and THF^+.

In the photolysis of Cp_3UR obtained by treating Cp_3UCl with LiR "in situ", there are complications. Excess of LiR apparently induces a thermal reduction, or other irreversible reaction, of Cp_3UR as reflected by the appearance of various unexpected signals in the NMR spectrum. This phenomenon is at present under further investigation [22]. If, in order to avoid this complication, a slight excess of Cp_3UCl (ca. 30—50%) is chosen for the formation of Cp_3UR, the Cp_3U^{III} species produced during the photolysis apparently interacts with the remaining Cp_3UCl to display a common "exchange resonance peak" in the range 10 to 20 ppm (room temperature), the actual position depending on the relative concentrations of the two species. At —70°C this "exchange peak" is reversibly split into two singlets at 14.1 and 36.0 ppm, and these paramagnetic shifts are characteristic of the two components Cp_3UCl and "species B" [3] at this temperature.

TABLE 1

SIGNIFICANT CHANGES IN THE NIR/VIS ABSORPTION SPECTRUM (peak positions in cm^{-1}) OF COMPLEX II IN THF ON LIGHT IRRADIATION (ca. 12 h). ABSORPTIONS OF UNCHANGED INTENSITY HAVE BEEN OMITTED

Absorption of starting complex II	Rate on irradiation	New absorption of final system	Cp_3U/Et_2O [4]
7.479s	disappears	7.353w	7.353m
8.475m-s	increases	8.418s	8.475s
8.749w	disappears		
9.294 m-s	disappears	9.200w	
9.699m-s	disappears	9.634m(sh)	9.524m(sh)
9.970m-s	increases		9.804m
10.776s	increases	10.811vs	10.929w
12.285w	increases		

Interestingly, Vasil'ev et al. have observed a stable adduct of Cp_3UCl and $(C_2H_5)_3Al$ [21] as well as a rapid transalkylation reaction between Cp_3UR and R'_3Al systems [19], while Kanellakopulos et al. have described the adduct $Cp_3U^{IV}F \cdot U^{III}Cp_3$ which is formed from $[Cp_3UF]_\infty$ and $Cp_3U \cdot THF$ [23]. It therefore appears reasonable to assume an adduct "$Cp_3UCl \cdot UCp_3$" of similar stability and even better solubility in THF than the fluorine-bridged homologue. It is not unlikely that in the presence of such an adduct the solubility of the competing adduct $Cp_3U \cdot THF$ would be reduced.

It seems noteworthy that apparently the same sequence of intermediates is observed after the photo-induced homolysis of Cp_3UR and during the reported reduction of Cp_3UCl by $LiAlH_4$ (signals of the "species A and B" have been noticed even during reaction with $LiBH(C_2H_5)_3$, where the final product is the U^{IV} derivative $Cp_3UOC_2H_5$) [3]. It is therefore not unlikely that corresponding features might also be detectable when Cp_3UCl is reduced with Na/naphthalene [2] or NaH [4].

Table 1 shows sections of the NIR/VIS optical absorption spectrum of complex II which displays characteristic changes after ca. 12 h of light irradiation. Although the final spectrum resembles those of both "species A" [3] and Cp_3U in $(C_2H_5)_2O$ [4], a final assignment to either of the two would not be justified.

Discussion

The results presented above indicate convincingly that the photo-reduction of Cp_3UR systems differs substantially from the photo-reduction of Cp_3ThR systems as far as the optimal reaction conditions, the nature and number of probable intermediates, the chemical composition of the resulting hydrocarbons and the mechanism of the overall reaction are concerned. One of the most significant features is that the initial step appears to be a homolytic scission of the U—C σ-bond, as evidenced by the observation of alkyl radicals by the spin trap technique, and by analyses of the resulting hydrocarbons. By comparison with the well-described pure thermolysis of Cp_3UR in aromatic solvents [14] on the one hand, and the clean photolysis of Cp_3ThR in benzene [10] on the other, the photolysis of Cp_3UR at elevated temperatures appears to be more related to the former rather than to the latter process. Particular interest is therefore focused on the question of to what an extent the photolysis of Cp_3UR-systems is comparable with the pure thermolysis.

The role of THF as a useful solvent for the photolysis seems to be twofold: first, there is a significant decrease of the stability of the U—C σ-bond (relative to that for solutions in toluene) which facilitates the U—C bond scission and allows use of relatively moderate reaction conditions. Thus, from our own results in THF solution and appropriate data in ref. 14, the barrier of activation for the purely thermal bond cleavage is roughly estimated to be lowered by a factor of 0.8. This feature is also underscored by recent findings of Razuvaev et al., who have noticed that e.g. the redox (or transalkylation) process: $2\ Cp_2V^{III}CH_3 + Cp_2V^{IV}Cl_2 \rightarrow Cp_2V^{IV}(CH_3)_2 + 2\ Cp_2V^{III}Cl$ is significantly affected by the formation of methane when the solvent cumene is replaced by THF [24].

Secondly, THF is well-known to stabilize considerably not only polar intermediates as carbanions, carbenes etc. [25], but likewise in situ generated radicals and radical pairs [26,27]. In particular, it has been known for more than a decade that in suitable solvents a substrate molecule or radical pair can be effectively enclosed by a cage of solvent molecules. It is customary to distinguish between various types of solvent cages, i.e. "cage pairs", "extended cage pairs", "solvent-separated pairs", etc., and equilibria between those different species [26]. A main difference between such strongly solvated radical pairs is the actual number of solvent molecules separating the two caged radicals from each other.

In view of the above results, it is suggestive to assume for the thermal homolysis of Cp_3UR in toluene the occurrence of highly constrained "cage pairs", or even of a concerted "cyclic reaction" [26] * without any radical formation, while the U—C bond cleavage in THF solution seems to afford "extended cage pairs" and "solvent-separated pairs", respectively. As photo-assisted homolysis of I in THF-d_8 leads to a clearly larger proportion of CH_3D than thermolysis in the same solvent, it seems reasonable to postulate a "solvent-separated pair" (i.e. a cage involving more than one solvent molecule between the two radicals as essential for the reaction under irradiation.

Purely thermal reaction in THF would then involve solvent cages with a relatively lower number of solvent molecules between the two radicals. Hence, light quanta might not only influence the cleavage of U—C and C—H bonds, but could likewise favour the transition of "extended cage pairs" into "solvent-separated pairs". Owing to the influence of light, both species might be also considered as photo-excited (i.e. not in thermal equilibrium with their surroundings).

The assumption of "extended" and/or "solvent-separated" pairs is further supported by the observation of extremely small amounts of free radical dimerization products ($2R^{\cdot} \rightarrow R—R$) as well as of olefinic species produced by H-atom transfer from $R^{\cdot}$ (= n-butyl) to either another radical $R^{\cdot}$ or to "$Cp_3U^{\cdot}$". The presence of solvent-free solid II yields markedly increased the ethane/methane ratios. Furthermore, Hackelberg and Wojcicki have recently demonstrated that

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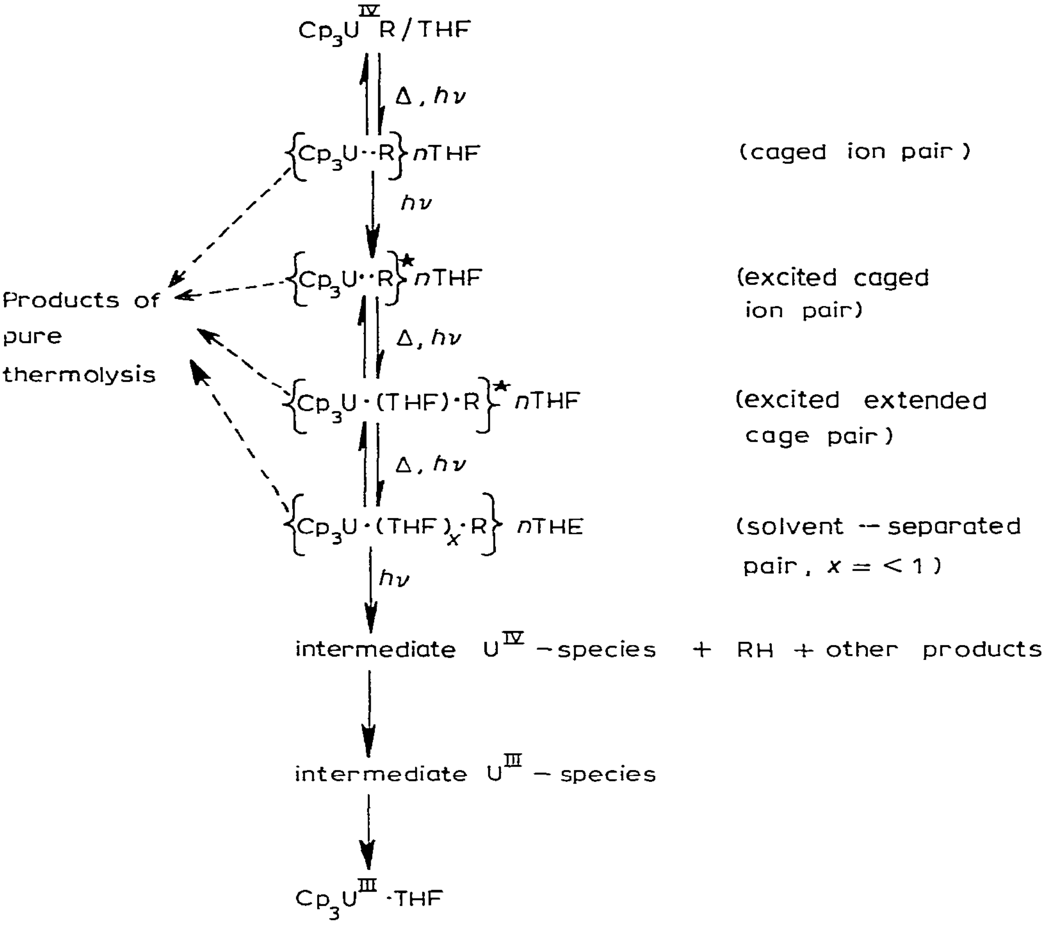
* A possible involvement of short-lived solvent cages in pure thermolysis of Cp_3MR (M = U, Th) was already considered by Marks et al. [14,28].



Scheme 1. Possible sequence of reaction steps, and intermediates, for the thermal photolysis of Cp_3UR in THF solution. The designation of single steps as "photoreactions", and of intermediates as "photo-excited", is very tentative.

methyl radicals generated during the photolysis of the complex $CpPt^{IV}(CH_3)_3$ in various non-coordinating solvents take up H atoms with very little selectivity from solvent molecules, Cp ligands and metal-bonded CH_3 groups [29]. These findings contrast with the CH_4/CH_3D ratios obtained on homolysis of I which in neither case (i.e. with and without light) agree with the statistical expection.

Obviously, the complete photo-assisted reduction of $Cp_3U^{IV}R$ to solvated Cp_3U^{III} must involve a multi-step process, the various stages of which require further clarification (Scheme 1). Thus, it is tempting to suggest a well-soluble and reactive species Cp_3UH as an intermediate before any genuine Cp_3U^{III}-system appears; however, authentic Cp_3UH is known to be thermally quite stable and only sparingly soluble, at least in toluene [13].

Another possibility would involve the transitory occurrence of an adduct $\{Cp_3U—H\cdots UCP_3\}$ which might explain the observation of the adduct $Cp_3U \cdot THF$ only at a rather late stage of the reaction. Although any direct evidence for the existence of a species $\{Cp_3U—H\cdots UCp_3\}$ is lacking, it is noteworthy that the novel system $Cp_3ZrH \cdot Al(C_2H_5)_3$ was recently prepared, and subjected to a crystallographic X-ray study [30]. The well-confirmed linear ZrHAl-alignment (ZrAl: 366 pm) in this complex in which all three Cp ligands are η^5-bonded, as well as the very pronounced Lewis-acidity of Cp_3U [1,23] suggest that a related uranium system $\{Cp_3U—H\cdots UCp_3\}$ could also exist.

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